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THE EFFECT OF ZIRCONIUM ON THE STRENGTH OF THORIUM

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The effect of zirconium on the strength of thorium

by

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ABSTRACT

The flow stress of thorium-zirconium alloys containing up to 12 atomic percent zirconium was studied over a range of temperatures and strain rates. It was found that the flow stress could be broken into a thermally activated and an athermal component. The thermally activated component was nearly the same in the base metal and the zirconium alloys. The major effect of zirconium was a considerable increase in the athermal component. The magnitude of this increase was directly proportional to the zirconium content. Zirconium also retarded the recovery and recrystallization processes.

INTRODUCTION

Thorium may become one of the most important metals used by man because of its potential role in nuclear reactors. It is capable of being transmuted to U^{233} which is a fissile isotope. It is also more abundant in the earth's crust than uranium; however, pure thorium has a low tensile strength and develops serious creep problems at the operating temperatures of nuclear power reactors. Consequently, there is a need to develop thorium alloys which are satisfactory from both the strength and nuclear aspects if thorium metal is to be put to use as a nuclear fuel material.

Hammond¹ has summarized some mechanical properties of thorium and its alloys. Most of the work that has been done in this area has only been concerned with engineering properties at room temperature and many of the results of these studies have been significantly influenced by high impurity contents. Skaggs² studied the effect of carbon on the strength of thorium from 4.2°K to 573°K over a range of strain rates. Nitrogen in thorium is presently being studied by McLachlan.³ Substitutional solute strengthening in thorium has received very little attention over a range of temperatures and strain rates. The thorium-zirconium system has a significant concentration range in which the effect of zirconium, a substitutional solute, on the strength of thorium can be studied. The complete thorium-zirconium phase diagram has been studied by

Gibson, Loomis, and Carlson⁴ who set the solubility of zirconium in alpha thorium at 14.4 atomic percent at 910°C. Johnson and Honeycomb,⁵ and Evans and Raynor⁶ have redetermined the solubility limit setting it at about 9.6 atomic percent zirconium at 900°C. Zirconium has a low thermal neutron capture cross section which would make its use in thorium alloy fuels practical. From a nuclear engineering standpoint, a systematic and comprehensive study of the effect of zirconium on the strength of thorium should be useful.

Solid solution alloys are stronger than the pure components of which they are composed. Results of studies on different alloys, however, indicate that the mechanism of strengthening is not always the same. It is known that solute segregation around dislocations, local order, long-range order, and solute valency often contribute to hardening of solid solutions as well as a random distribution of solute (simple solution-hardening). Consequently, a number of different theories have been proposed to explain solid solution hardening.

One of the first theories on simple solid solution hardening was developed by Mott and Nabarro^{7,8} who assumed that the increase in strength in substitutional solid solutions was due to frictional resistance encountered by the edge component of a moving dislocation. This frictional resistance was due to the elastic interaction between a dislocation and the isolated

elastic stress field set up by the difference in size between a solvent and solute atom. By considering concentration, difference in size through a misfit parameter, and estimating what they felt to be reasonable maximum and minimum lengths of a moving dislocation loop, they derived expressions for the upper and lower limits of the critical shear stress to be expected. McLean⁹ and Cottrell¹⁰ have compared experimental results with calculations from this theory for various metals and found predicted values to be too high. Fleischer^{11,12} in developing a theory on simple solid solution hardening has criticized the Mott and Nabarro theory because it does not include interactions between screw dislocations and the stress fields set up by different sized solute atoms or dislocation-solute atom interactions due to different stiffnesses of solute atoms which act as either hard or soft spots in the matrix. Fleischer has pointed out that the volume expansion associated with a screw dislocation as shown by Stehle and Seeger¹³ does lead to an interaction between solute atoms and screw dislocations. His theory includes this interaction along with moduli effects of solute atoms in arriving at solution hardening as

$$\Delta\sigma = Z_1 \cdot G \cdot C^{1/2} \cdot \epsilon^{3/2}$$

where

G is the shear modulus of the matrix,

Z_1 is a constant, theoretically calculated to be equal to 1/760 for interaction with screw dislocations;

ϵ is a parameter combining difference in size and modulus between solute and matrix atoms.

He has shown that in the case of copper base alloys, the $3/2$ exponent is in good agreement with experimental results and concluded that elastic interactions between dislocations and solute atoms are mainly due to difference in size and modulus effects. Other studies testing Fleischer's complete theory are lacking probably because of the considerable amount of data needed in determining ϵ for a series of different solutes. Studies have indicated that the variation of stress with concentration to the $1/2$ power is not always realized.

There is good reason to believe that the valency of a solute atom affects solution hardening. The elastic strain field of an edge dislocation results in the creation of a line dipole. This occurs because conduction electrons tend to move from the region of compression to that of tension. This results in an electrical interaction between the edge component of a dislocation and the valency of a solute atom. Ainslie and co-workers¹⁴ showed that copper-base alloys of aluminum, zinc, and silicon have equal yield strengths for similar electron to atom ratios; however, this criteria failed for copper-tin alloys.

Short and long range ordering influence the deformation characteristics of solid solutions. Fisher¹⁵ was first to discuss the hardening to be expected from short range order.

He suggested that local order would exist in many solid solutions because the neighbors of a small atom would be larger ones more often than in a purely random alloy, and that neighbors of large atoms would tend to be small ones. The motion of a dislocation would diminish the degree of order, which raises the energy, and this would be reflected in a higher yield stress. This mechanism should have a decreasing effect on the strength with increasing strain. Once a dislocation cuts an ordered region, order in that region should be largely destroyed and resistance to following dislocations decreased. The deformation of long-range ordered alloys is particularly interesting. There is evidence¹⁶ that dislocations often move in pairs in these alloys. This occurs because the order destroyed by a leading dislocation is restored by its following dislocation. These pairs are commonly referred to as "superdislocations".

In the theories discussed so far, the hardening has been attributed to the resistance that a moving dislocation encounters in a homogeneous solid solution. Cottrell and Bilby¹⁷ proposed a theory for the sharp yield point observed in mild steel by the locking of mobile dislocations by carbon atoms. They showed that carbon atoms would prefer to occupy sites in the dilated region along an edge dislocation thereby reducing the internal strain energy of the crystal and exerting a locking force on the dislocation until the applied stress was

high enough to tear the dislocation from its carbon atmosphere. Once freed, the dislocation could move at a reduced stress and result in a sharp drop in load. This theory has been criticized on the basis that new dislocations might be generated before locked dislocations escape their atmospheres. In either case, such a mechanism offers a feasible explanation for the yield point and can be extended to explain strain aging.

Mobile dislocations can become locked during no-load periods by the diffusion of carbon to free dislocations and cause the return of the yield point. The Cottrell-Bilby theory is quantitatively concerned with carbon in iron, but its basic principles can be extended to solid solutions with substitutional solutes. Yield points have been observed in substitutional solid solutions though their existence is not as pronounced as those in steel. Suzuki¹⁸ has developed a similar theory for metals with close packed structures. In these metals, dislocations often split into two partials connected by a stacking fault. Suzuki has reasoned that since the structure in the faulted region differs from that in the matrix, the equilibrium concentration of solute atoms should also be different. This would create a locking force on the partial dislocations since any movement would result in a nonequilibrium stacking fault concentration and increase the energy of the crystal. This mechanism offers a conceivable alternative explanation for yield points as well as strain aging observed in metals with

close packed structures.

Random thermal fluctuations can aid the force on a dislocation in overcoming short-range obstacles during the application of a stress. Micro-processes which are believed to occur due to the combined effect of stress and thermal fluctuations are: 1) nonconservative motion of jogs, 2) cross-slip of extended dislocations, 3) overcoming of the elastic interaction between dislocations and impurity atoms, 4) interaction of forest dislocations, 5) climb, 6) overcoming the Peierls-Nabarro force. According to Conrad¹⁹ when one or more such processes are active, the flow stress can be assumed to be the sum of an athermal component, σ_{μ} , which depends on temperature through the shear modulus, μ , and a thermally activated component, σ^* , which depends on temperature, and strain rate; i.e.

$$\sigma = \sigma^*(T, \dot{\gamma}) + \sigma_{\mu}.$$

Concentration and strain can also affect the athermal and thermally activated component.² Friedel²⁰ has analyzed thermally activated unpinning of dislocations in random solid solutions and developed expressions for the athermal and thermally activated components of stress, activation energy, and activation volume for two cases: not too dilute and very dilute solutions.

Skaggs² compared experimental results with predictions from this theory and found it to be a fair description of the deformation properties of thorium-carbon alloys. His work is

particularly interesting since it shows thorium-carbon alloys to be strongly temperature and strain rate dependent. Though this phenomena is not entirely unique, strong temperature and strain rate dependence is normally not observed in face centered cubic metals. Body centered cubic metals often show strong temperature and strain rate dependence. Consequently much consideration has been given to the structure in explaining this difference. Like the strong temperature and strain rate dependence, the yield point in thorium-carbon alloys is somewhat unusual in face centered cubic alloys. Instead of being characterized by a sharp drop off in load, the upper yield point is reached only after 0.001 to 0.005 plastic strain. The flow curve then decreased smoothly to a minimum before it is increased by work hardening. Thorium is therefore a very interesting metal from an alloy hardening point of view and it was felt that a study of the effect of a substitutional solute on its strength might very well add to our understanding of this field.

In this study the flow stress of four polycrystalline thorium-zirconium alloys was measured at temperatures ranging from 4.2°K to 873°K. The effect of zirconium content, grain size, strain rate, strain, and temperature on the strength was determined from these measurements.

EXPERIMENTAL PROCEDURE

Preparation of Specimens

The thorium used in this study was prepared by the magnesium intermediate alloy method described by Peterson et al.²¹ and had the analysis given in Table 1. The zirconium was reactor grade crystal bar zirconium. Three thorium-zirconium alloys (nominal composition 4.0, 8.0 and 12.0 atomic percent) were made by arc-melting a weighed amount of zirconium and fifty grams of base thorium into a button. These buttons were turned over and remelted four times to insure a uniform zirconium distribution. They were then melted into elongated ingot molds six inches long by three-fourths inch diameter. A fifty gram base metal ingot was also prepared in the same manner. The base thorium and alloy ingots were subsequently cold swaged to 0.097 inch diameter rods and cut into two inch long segments.

Table 1. Analysis of thorium used in this study

Element	Content, ppm	Element	Content, ppm
C	30	Mg	<20
O	88	Mn	<20
N	20	Ni	<20
Al	~ 20	Ta	54
Ca	<20	Ti	N.D.
Cr	<20	W	10
Fe	<20	Y	N.D.

Specimens for recrystallization and recovery studies were prepared by cutting the as-swaged rods of each composition into one-fourth inch long pieces. Each piece was cleaned in a hot nitric acid-sodium fluosilicate solution to remove the oxide surface layer, annealed one hour under a dynamic vacuum, and furnace cooled. Dynamic vacuum annealing was used so that any hydrogen in the specimens would be evolved as shown by Peterson and Westlake.²² Each annealed specimen was subsequently mounted and a longitudinal section electropolished and electroetched. Electropolishing was done in a methyl alcohol-6% by volume perchloric acid electrolyte at -70°C using D.C. potential of fifty volts. Electroetching was done in a 50% phosphoric acid-50% by volume acetic acid electrolyte at six D.C. volts. The etched surface was metallographically examined and the diamond pyramid hardness measured.

Tensile specimens were prepared by electropolishing two inch long specimens to 0.095 inch diameter. The 0, 4.0 and 8.0 percent alloys were annealed under a dynamic vacuum at 900°C for one hour and the 12 percent alloy at 1000°C for two hours followed by 900°C for one hour. Annealed samples were normally quenched into water so that the zirconium would be retained in solution in the alpha-thorium. Some specimens were furnace cooled to determine the effect of quenching on the hardness and strength. The center one inch of the annealed specimen was electropolished to a reduced diameter of 0.090 ± 0.001 inches. This left one-half inch at each end of the

specimen to be gripped by a serrated four jaw collet, which in turn, was compressed by a tapered compression nut. This arrangement was satisfactory in that no slippage occurred in the grips, deformation outside the reduced one inch gage length was negligible, and the notches created by the grip did not cause fracture in the grip section. The annealed 0, 4.0, and 8.0 percent zirconium tensile specimens had uniform, equiaxed, single phase grains of approximately 1200, 2500, and 3700 grains per square millimeter respectively. The 12 percent alloy after quenching consisted of an alpha thorium matrix with grains of quenched beta phase. The beta phase was mainly located between alpha grains and the volume percent of transformed beta was metallographically determined to be 6.5 percent. The alpha thorium matrix was exceptionally fine-grained with 7500 grains per square millimeter.

Since the chemical analysis of the alloys gave results which differed from the nominal compositions more than what was expected, precise lattice parameters of the base metal and alloys were determined to give further information as to the zirconium content of the alloys. Quenched polycrystalline rods were electropolished to 0.005 inch diameter and the lattice parameter determined using a 114.6 millimeter diameter Debye-Scherrer powder camera. For the nominal compositions of 0, 4.0, and 8.0 percent, the lattice parameters agreed to within $0.002\text{\AA}$ or less of values given by Johnson and Honeycomb⁵ for

similar compositions. If the analytical values of 0, 4.6 and 9.2 percent are used, the agreement is to within $0.005\text{\AA}$. The lattice parameter of the 12.0 percent alloy indicates a zirconium solubility of 10.5 atomic percent according to Johnson and Honeycomb.⁵ Results of tensile tests and resistivity measurements further supported the nominal compositions. Accordingly, the nominal compositions were used throughout this paper.

Tensile Tests

The tensile machine used in this investigation was a screw driven Riehle Model FS-10 Universal Screw Power Tensile Testing Machine. The lower crosshead speed range was from 0.002 to 2.0 inches per minute and was found to be accurate to within ± 10 percent. The load was accurate to within ± 1 percent. Since the specimen was submerged in various media to maintain temperature, a Riehle Model DC Deflectometer was used to measure the motion of the lower crosshead. The deflectometer, which incorporates the use of a linear differential transformer, sends an electrical signal to a Riehle Model RD-5 Recorder which traces the load as a function of lower crosshead motion. From this trace, the true stress and true strain were determined by taking into account the elastic contribution of the tensile testing apparatus.

Low temperature tests were carried out in a cryostat similar to that used by Kaufman and co-workers.²³ This apparatus basically consists of a compression tube which is fastened to

and extends below the lower crosshead and a pull rod which is fastened to the upper crosshead and extends down partly through the compression tube along the tube axis. The top and bottom of the specimen are held by grips fastened to the bottom of the pull rod and compression tube respectively. When the lower head moves down, a tensile load is applied to the specimen. The temperature of the specimen is controlled by containing the compression tube within a Dewar and maintaining the liquid level above the specimen.

Since thorium oxidizes readily at high temperatures, high temperature tests were carried out under an argon atmosphere using a similar apparatus shown in Fig. 1. The compression tube was contained in a cylindrical resistance furnace and contained no holes in the sides. An argon gas atmosphere was continually maintained under a slight positive gage pressure through the housing at the top of the compression tube. Two thermocouples were also introduced through the same opening in the housing and measured the temperature next to the top and bottom of the one inch gage length of the specimen. The temperature difference between these two points was 15°C at 200°C, 10°C at 400°C, and 5°C at 600°C and the average temperature could be maintained to within 1°C during the course of a run. The oxidation of a specimen was found to be negligible.

Figure 1. Schematic view of high temperature testing apparatus

RESULTS AND DISCUSSION

Recovery and recrystallization kinetics of the thorium base metal and thorium-zirconium alloys were studied in order to determine a suitable annealing temperature at which to anneal the swaged specimens to produce strain free, equiaxed grains. It was found that the addition of zirconium to alpha thorium retarded the rate of recovery and increased the recrystallization temperature. Figure 2 shows the diamond pyramid hardness-annealing temperature curves for each composition. Each point is the average of five or more hardness tests taken on a small specimen which was first annealed one hour at temperature, furnace cooled, and metallographically examined. It is clearly seen that the addition of zirconium significantly retards the rate of recovery. The anomalous behavior of the 12 atomic percent alloy at 600°C was probably due to precipitation from this supersaturated solid solution. The microstructure of these specimens showed that zirconium retarded recrystallization and refined the grain size. Uniform equiaxed grains were first observed in the base metal, 4.0, and 8.0 atomic percent alloys at 700°C, 900°C, and 900°C respectively. The 12 atomic percent alloy did not show signs of recrystallization until heated to 900°C and had to be annealed two hours at 1000°C before all microstructural evidence of work hardening was gone.

Since the grain size varied between the alloys, the

Figure 2. Room temperature diamond pyramid hardness after one hour anneal at temperature

effect of grain size on the strength was determined. A comprehensive study was not made however because of the difficulty in producing coarse grain sizes in the zirconium alloys. It was found that the flow stress of the zirconium alloys includes some contribution due to the finer grain size of these alloys. Coarse grained base metal and 4.0 atomic percent zirconium specimens were produced by heating forty-nine hours at 1100°C, and quenching into water. The 8.0 atomic percent alloy was heated at 1050°C for 165 hours. The 12.0 atomic percent alloy was not coarsened by either of these treatments due to the presence of beta phase at both 1050°C and 1100°C. The coarse grained specimens were then annealed at 900°C for two hours under a dynamic vacuum to evolve hydrogen from the specimens²² and quenched into water. The grain size of the coarse grained base metal was 44 grains per square millimeter. It was found that at 300°K the 0.2 percent offset flow stress of this specimen was 7,770 psi while that of the fine grained base metal specimen (1200 grains per square millimeter) was 7,860 psi. This indicates that grain size does not affect the yield strength of pure thorium, especially in light of the fact that the large grained specimen exhibited a perfect manifestation of a chisel edge fracture; and when metallographically examined, displayed an enormous grain embracing the entire cross-section of the specimen in the fractured region. The flow curve of the fine grained 4.0 atomic percent specimen (2500

grains per square millimeter) displayed an upper yield point of 15,200 psi. When the nearly linear portion of the flow curve was extrapolated back to the elastic region thus disregarding the yield point effect, the 0.2 percent offset flow stress was 14,000 psi. The large grained 4.0 atomic percent specimen (425 grains per square millimeter) did not display a yield point and the 0.2 percent offset flow stress was 11,700 psi. The flow curve of the fine grained 8.0 atomic percent specimen (3700 grains per square millimeter) displayed an upper yield point of 22,800 psi and an extrapolated 0.2 percent offset flow stress of 21,000 psi. The large grained 8.0 atomic percent specimen (1025 grains per square millimeter) did not display a yield point and the 0.2 percent offset flow stress was 19,900 psi.

The effect on strength of cooling rate from the annealing temperature was determined. A base metal, 4.0, and 8.0 percent alloy specimen was annealed one hour at 900°C, furnace cooled, and tested at 300°K. The resulting true stress-true strain curves were identical within the accuracy of the measurements to those of the corresponding quenched specimens.

The resistivity of a random solid solution should increase linearly with atomic percent solute.²⁴ The results of resistivity and resistance ratio measurements made on the base metal and thorium-zirconium alloys followed this behavior. The room temperature resistivity was determined by passing a

current through a specimen of uniform cross section, measuring the voltage difference between two points one inch apart, and calculating the resistivity. The resistance ratio at 4.2°K and 78°K was determined by measuring the voltage difference at room temperature, in liquid nitrogen and in liquid helium and calculating $V_{300^\circ\text{K}}/V_{4.2^\circ\text{K}}$ and $V_{300^\circ\text{K}}/V_{78^\circ\text{K}}$. The accuracy of the resistivity measurement and resistance ratio was about three percent. Figure 3 shows the variation of resistivity with temperature to be nearly linear. The variation of resistivity with zirconium content was found to be linear between zero and eight atomic percent zirconium and independent of temperature which indicates that Mathiessen's rule is obeyed for single phase alpha thorium-zirconium alloys and that zirconium atoms are dispersed randomly in alpha thorium. The resistivity of the 12.0 atomic percent alloy at room temperature was equal to what would be expected for a single phase alpha thorium-zirconium alloy with 10.6 atomic percent zirconium in substitutional solid solution. The 12.0 atomic percent alloy decreased abruptly in resistivity at 6.3°K. This was due to the presence in this alloy of 6.5 volume percent beta phase containing 65 atomic percent zirconium which becomes superconducting at 6.3°K. The resistivity of a 12.0 atomic percent alloy quenched from the beta phase at 1200°C is shown in Figure 3. The structure of this specimen was strained face centered, cubic²⁵ produced by transformation of the beta phase.

Figure 3. Resistivity vs. temperature

It behaves as would be expected for a single phase alpha thorium-12 atomic percent zirconium alloy.

The flow stress of the base metal and thorium-zirconium alloys was found to be dependent on temperature, zirconium content, strain, and slightly on strain rate. Figure 4 shows the flow stress at two percent plastic strain as a function of temperature. The flow stress at two percent plastic strain was used rather than the 0.2 percent offset stress because at smaller strains the flow curve was often affected by a yield point. These flow stress-temperature curves are similar to those that have been obtained by other investigators studying thorium and thorium alloys who divided the flow stress into a thermally activated and athermal component.

Klievoneit²⁶ studied the plastic properties of Ames thorium containing 410 ppm carbon, 1300 ppm oxygen, and 70 ppm nitrogen from 77°K to 1173°K. His flow stress-temperature curves showed that from 77°K to 423°K the flow stress was dependent on temperature, from 423°K to 673°K it was essentially independent of temperature, and above 673°K it was once again temperature dependent. Also in the temperature dependent regions he found that the flow stress varied with strain rate. He pointed out that his experimental results agree quite well with those predicted by Schoeck²⁷ who suggested that the temperature and strain rate dependence of flow stress at temperatures below the nearly temperature independent region of flow

Figure 4. Flow stress at 2% strain vs. temperature

stress is due to thermal activation of dislocations in surmounting obstacles to dislocation movement. At 423°K and above, thermal activation would be instantaneous and only the athermal stress hindering dislocation movement would be observed. The very small temperature dependence between 423°K and 673°K was due to the fact that the athermal stress is related to the shear modulus which decreases slightly with increasing temperature. The reoccurrence of the strain rate and temperature dependence above 673°K was due to recovery processes in that less time for recovery to occur is allowed at a higher strain rate and more strain hardening accumulates.

Skaggs² made a comprehensive and systematic study of thorium metal and thorium-carbon alloys containing from 4 to 1500 weight ppm carbon between 4.2°K and 573°K. The flow stress-temperature curves were similar to those of Klievoneit and could be divided into a low temperature region where the flow stress was temperature dependent and an intermediate temperature region where the flow stress was almost independent of temperature. He also observed strain-rate dependence in the low temperature dependent region. The flow stress was expressed as the sum of a thermally activated and athermal component of stress. The thermally activated component was that contribution to the flow stress that gave rise to the temperature and strain rate dependence of flow stress in the low temperature region. It increased linearly with carbon content

and was attributed to randomly dispersed carbon atoms in solid solution setting up barriers to dislocation movement and the overcoming of these barriers by the force on a dislocation aided by thermal fluctuations. Work by Skaggs indicated that the temperature and strain rate dependence of flow stress in Klievoneit's²⁶ study was mainly due to the carbon content of Ames thorium. The athermal component, considered to be due to the interaction of dislocations and long range obstacles increased with carbon content and decreased slightly with temperature. The thermally activated component was significantly larger by a factor of seven at 4.2°K and 2 percent strain than the athermal component.

Each composition in Figure 4 displays a temperature dependent region in approximately the same temperature region as that observed by Klievoneit²⁶ and Skaggs,² namely 0°K to 423°K. From 423°K to 673°K the flow stress varies only very slightly with temperature, and at higher temperatures is once again temperature dependent. The flow stress was observed to be strain rate dependent in the low and high temperature regions. It should be appropriate then to consider the flow stress of the base metal and thorium-zirconium alloys in this study as the sum of a thermally activated and athermal component of stress between 0°K and 673°K.

The base metal used in this study contained a certain amount of carbon, nitrogen and oxygen. These produced a significant thermally activated component of the flow stress.

If the strength contribution from nitrogen and oxygen found by Skaggs were added to the contribution from carbon based on the carbon content of this base metal, a flow stress of 27,000 psi at 4.2°K would be predicted and a flow stress of 26,000 psi was found. The temperature dependence of the 4.0 atomic percent alloy was less than that of the base metal which indicated that the thermally activated component was smaller in the 4.0 percent alloy than in the base metal. The temperature dependence increased slightly when going from 4.0 atomic percent zirconium to higher concentrations which indicated that the addition of zirconium contributed to the thermally activated component of flow stress. An explanation for this behavior is that the addition of zirconium to the base metal nullified, at least in part, the contribution of impurities to the thermally activated component of stress and added a small thermally activated component due to the presence of zirconium atoms in substitutional solid solution.

This explanation was supported by measurements of the strain rate dependence of the flow stress in the low temperature region. The strain-rate parameter, $\Delta\sigma/\Delta\ln \dot{\epsilon}$, was difficult to measure because it was small. Often a change in the strain rate produced a change in load hardly as large as the width of the line tracing the load-elongation curve. Table 2 lists the strain-rate parameter at 2.0 percent offset for the various temperatures. The addition of 4 percent zirconium

Table 2. Strain-rate parameter (pounds per square inch) measured at 2.0 percent plastic strain

Temp. °K	Atomic percent Zr			
	0	4	8	12
4.2	0	0	0	0
78	220 $\pm$ 90	210 $\pm$ 90	170 $\pm$ 90	350 $\pm$ 90
196	440 $\pm$ 90	310 $\pm$ 90	390 $\pm$ 90	600 $\pm$ 90
300	590 $\pm$ 90	120 $\pm$ 90	200 $\pm$ 90	200 $\pm$ 90
473	50 $\pm$ 40	0	0	0
673	50 $\pm$ 40	0	0	0
873	220 $\pm$ 90	210 $\pm$ 90	800 $\pm$ 90	1200 $\pm$ 90

slightly decreased the strain rate parameter and further additions of zirconium slightly increased this parameter. Zirconium did not show a large effect on the thermally activated component. The strain rate parameter did not change significantly with strain.

The dominant effect of zirconium is an increase in the athermal flow stress. This is shown in Figures 4 and 5 by the increased flow stress in the plateau above 423°K. The onset of recovery processes at 873°K can also be clearly seen in Figure 5. The flow stress at 473°K is plotted in Figure 6 as a function of zirconium content. This figure shows the effect of zirconium on the athermal component of flow stress since the athermal component is equal to the total flow stress at this temperature. The athermal component of stress increased linearly with zirconium content at both 2 and 15 percent

Figure 5. Flow stress at 15% strain vs. temperature

Figure 6. Flow stress vs. atom percent zirconium at 473°K

plastic strain for the base metal, 4.0, and 8.0 percent zirconium alloys. This linear behavior continued to 12.0 atomic percent zirconium at 2 percent strain. The flow stress of the 12.0 atomic percent alloy at 15 percent strain lies below a linear extrapolation to 12.0 atomic percent zirconium. Similar behavior was obtained at 673°K. In light of the 12.0 atomic percent alloy being two phase and the alpha thorium matrix in this alloy containing 10.5 atomic percent zirconium, linear behavior at either 2 or 15 percent strain was not expected for the 12.0 atomic percent alloy. The linear dependence of strength agrees with that predicted by Mott and Nabarro^{7,8} whose theory is based on the difference in size between solute and solvent atoms. It does not agree with Fleischer's theory^{11,12} which, in addition to size differences between atoms includes localized modulus effects of solute atoms and predicts the increase in stress to vary with the square root of the solute concentration.

The rate of strain hardening was found to decrease with increasing temperature and increase with zirconium content. The effect of temperature on the rate of strain hardening can be seen in Figures 7, 8, 9 and 10 which show that for each composition the rate of strain hardening decreases with increasing temperature. The decrease in the rate of strain hardening with temperature also accounts for the larger temperature dependence of the flow stress-temperature curves at 15 percent strain than

Figure 7. True stress vs. true strain, 0 percent zirconium

Figure 8. True stress vs. true strain, 4 atomic percent zirconium

Figure 9. True stress vs. true strain, 8 atomic percent zirconium

Figure 10. True stress vs. true strain, 12 atomic percent zirconium

at 2 percent strain. The change in flow stress between 2 and 15 percent strain is given in Table 3. It was found that at all temperatures, the rate of strain hardening increased slightly with zirconium content. At 473°K and 673°K, the rate of strain hardening continued to decrease with temperature in the base metal while the rate of strain hardening of the 4 and 8 percent alloy decreased very slightly. This indicates that the addition of zirconium retarded recovery at these temperatures and agrees with the results of the recovery and recrystallization studies.

Table 3. Change in flow stress (psi) between 2 and 15 percent plastic strain

Temp. °K	Atomic percent Zr			
	0	4	8	12
4.2	19000+400	21600+400	24600+400	31900+400
78	15800+400	17600+400	20500+400	19200+400
196	12000+400	14000+400	16900+400	14100+400
300	9400+400	12300+400	15400+400	12900+400
473	6400+400	11900+400	14900+400	13400+400
673	5300+400	11500+400	14300+400	15000+400
873	3110+400	6400+400	8100+400	4100+400

Since the 2.0 percent strain-flow stress was mainly used in this study to eliminate the effect of the yield point observed in some specimens and the 0.2 percent offset flow stress is often used as a design criteria, it was felt that a table of the change in stress between that at 2 percent strain

and an extrapolation from the nearly linear portion of the flow curve back to 0.2 percent strain would be useful. This information is given in Table 4. These differences are related to the initial slope of the stress-strain curve and are very nearly the same at all temperatures and compositions. The stress-strain curves all started with nearly the same slope but remained linear to higher strains at lower temperatures. The linear stress-strain behavior also persisted to higher strain for the zirconium alloys than for pure thorium.

Table 4. Change in flow stress (psi) between 0.2 and 2 percent plastic strain

Temp. °K	Atomic percent Zr			
	0	4	8	12
4.2	2300 $\pm$ 400	2900 $\pm$ 400	3000 $\pm$ 400	4400 $\pm$ 400
78	3400 $\pm$ 400	3400 $\pm$ 400	4000 $\pm$ 400	3600 $\pm$ 400
196	3300 $\pm$ 400	3300 $\pm$ 400	2600 $\pm$ 400	3400 $\pm$ 400
300	2900 $\pm$ 400	3200 $\pm$ 400	2900 $\pm$ 400	2200 $\pm$ 400
473	2950 $\pm$ 400	3300 $\pm$ 400	2700 $\pm$ 400	3500 $\pm$ 400
673	2400 $\pm$ 400	4000 $\pm$ 400	4300 $\pm$ 400	3300 $\pm$ 400
873	1190 $\pm$ 400	2150 $\pm$ 400	2400 $\pm$ 400	1700 $\pm$ 400

A small yield point, not shown in Figures 7, 8, 9, and 10, was observed in the fine grained thorium-zirconium alloys tested at certain temperatures. The base metal did not display a yield point except in the specimen that was furnace cooled. The yield point in the 4.0 atomic percent alloy was observed at 196°K and 300°K; in the 8.0 atomic percent alloy

at 196°K, 300°K, and 473°K; and in the 12.0 atomic percent alloy at 78°K, 196°K, 300°K, and 473°K. The upper yield point in the 4.0 percent alloy was rounded similar to that observed in thorium carbon alloys.² In the 8.0 percent alloy the upper yield point was sharp and dropped discontinuously at 473°K. The yield point was usually followed by one to two percent plastic strain at nearly constant stress similar to that observed in mild steel and which characterizes the Luder's band region. The flow curve of the large grained specimens indicated that large grain size eliminated the yield point. The effect of furnace cooling from the annealing temperature on the yield point of the zirconium alloys was very small.

The flow curves of the zirconium alloys tested at 4.2°K were serrated. The number of serrations per unit strain increased with strain and strain rate, and the change in stress associated with these serrations increased with strain and zirconium content. These serrations were characterized by a discontinuous drop in load from an otherwise smooth and normal flow curve. The flow curve of the base metal was smooth. Discontinuous yielding at 4.2°K has been observed in aluminum by Chin and co-workers,²⁸ in aluminum alloys by Kaufman and co-workers,²³ and at 20°K in AM 350 and AISI 304 stainless steels by Guntner and Reed.²⁹ In these studies local adiabatic heating was cited as the likely mechanism for serrated yielding. This mechanism suggests that the energy

released during plastic deformation in a localized region raises the temperature locally to a point where the strength in that region is less than when at the testing temperature. The result is a sudden increase in plastic strain and a decrease in load. Accordingly, a metal with a large temperature dependence of flow stress should display serrated yielding at very low temperatures more readily than a metal with a small temperature dependence. Figures 4 and 5 show that the temperature dependence of flow stress increases with zirconium content in the alloyed specimens which supports the adiabatic heating theory but a reversal takes place between the base metal and 4.0 percent alloy.

Relaxation studies were carried out on all tensile specimens. The results of these studies on the zirconium alloyed specimens tested at 473°K were particularly interesting. It was found that up to 10 percent plastic strain (region of relative large work hardening) continuation of deformation after a ten minute or more relaxation period resulted in a sharp yield point followed by 1 to 2 percent strain at constant flow stress before work hardening was again resumed. Figure 11 shows this behavior in the load-elongation curve for the 8.0 percent alloy tested at 473°K. The 4.0 percent alloy had no initial yield point and the yield point at the beginning of plastic deformation in the 12.0 atomic percent alloy was very small, yet both these alloys showed a yield point and discontinuous yielding following relaxation as in the 8.0 percent alloy. Figure 11

Figure 11. Load vs. elongation of the 8.0 atomic percent alloy tested at 473°K

shows the flow curve to become somewhat wavy in nature at higher strains at constant strain rate. This behavior was even more pronounced at 673°K and resembled the Portevin-LeChatelier effect observed in steel. At 873°K this behavior was absent and the flow curve was smooth for all alloys.

CONCLUSIONS

Between 4.2°K and 673°K, the flow stress of thorium-zirconium alloys can be resolved into a thermally activated and athermal component of stress. The thermally activated component was nearly the same in the zirconium alloys as in the base metal. The principal effect of zirconium was considerable increase in the athermal component. This increase in the athermal component was directly proportional to the zirconium content.

Zirconium retarded both the dynamic and static recovery processes. Consequently zirconium alloys showed a larger increment of strength due to work hardening at a given strain and maintained this work hardening to a higher temperature. Zirconium also retarded recrystallization and produced extremely fine grain sizes in the higher zirconium alloys. At 873°K all of the alloys exhibited recovery during testing and precipitation of zirconium from solutions.

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